Relation between Foaming Properties and the Structure of Surface Active Substances. I. Foaming Properties of Aqueous Soap and Sodium Dodecyl Sulfate

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Introduction

As was previously reported[1], the foaming power of aqueous sodium dodecyl sulfate (hereafter called SDS) is a function of concentration, and the critical micelle concentration (hereafter called cmc.) can be determined by this method. In a similar fashion, any other surface active substances may be closely correlated to the structure of its solution.

According to the foaming power measurement by Ross-Miles' method, the foaming power of SDS increases with concentration up to cmc. and above the cmc. it becomes nearly constant. In the light of this knowledge, the foaming power measurement of soap, a most typical surface active substance, carbon numbers of which range from ten to sixteen, was undertaken. The mechanism of foaming may be explained partly by Debye's theory[2] and at the same time by surface tension.

Since some inorganic ions are known to lower surface tension, the foaming properties of soap may be expected to be increased by the addition of those ions. In fact, the foaming power increases in the order of lyotropic series.

Experimental

Apparatus — The apparatus used is the same as that of Ross-Miles[3]. The schematic diagram and the dimension were described in the author's previous report[1]. For surface tension measurement DuNouy's tensiometer was used.

TABLE I

ANALYSIS OF FATTY ACIDS

Acid	M. P.		N. V.*	
	found	literature	found	theoretical
Capric	32.3	31.6	320.3	325.70
Lauric	45.1	44.2	278.0	280.09
Myristic	54.0	54.4	242.9	245.67
Palmitic	60.8	63.1	213.7	218.80

* N. V.......Neutralisation Value

Materials — The analysis of SDS was described in the previous report[1]. Soap used here is sodium salt of fatty acids which were prepared using fatty acids purchased from Merck and purified. The analysis is shown in Table I.

Inorganic salts, (LiCl, NaCl, KCl and RbCl) were all given by the courtesy of Dr. Y. Murakami, Faculty of Science, University of Tokyo.

Measurement — The temperature is kept by the thermostat at 40±0.1°C. All solutions are prepared under the same condition and the measurements are done right after the preparation of the solution, since soaps are very sensitive to temperature and time.

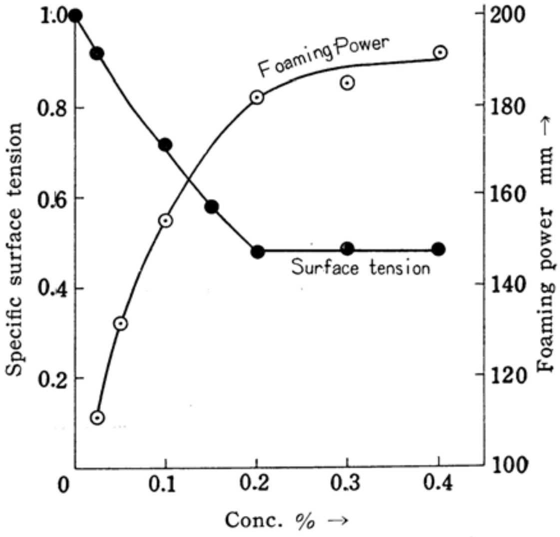

Fig. 1. Surface characteristics of sodium dodecyl sulfate.

Results

Fig. 1 shows foaming power (i. e. height of the foam part, expressed in mm) and specific surface tension against concentration of SDS. Specific surface tensions are calculated from values measured by DuNouy's tensiometer. By comparing these curves it can be seen that there is a correlation between foaming power and surface tension ; that is, as foaming power

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[1] M. Kashiwagi, This Bulletin, **29**, 193 (1957).
[2] P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575-92 (1949).
[3] J. Ross and G. D. Miles, *Oil and Soap.*, **18**, 99 (1941).

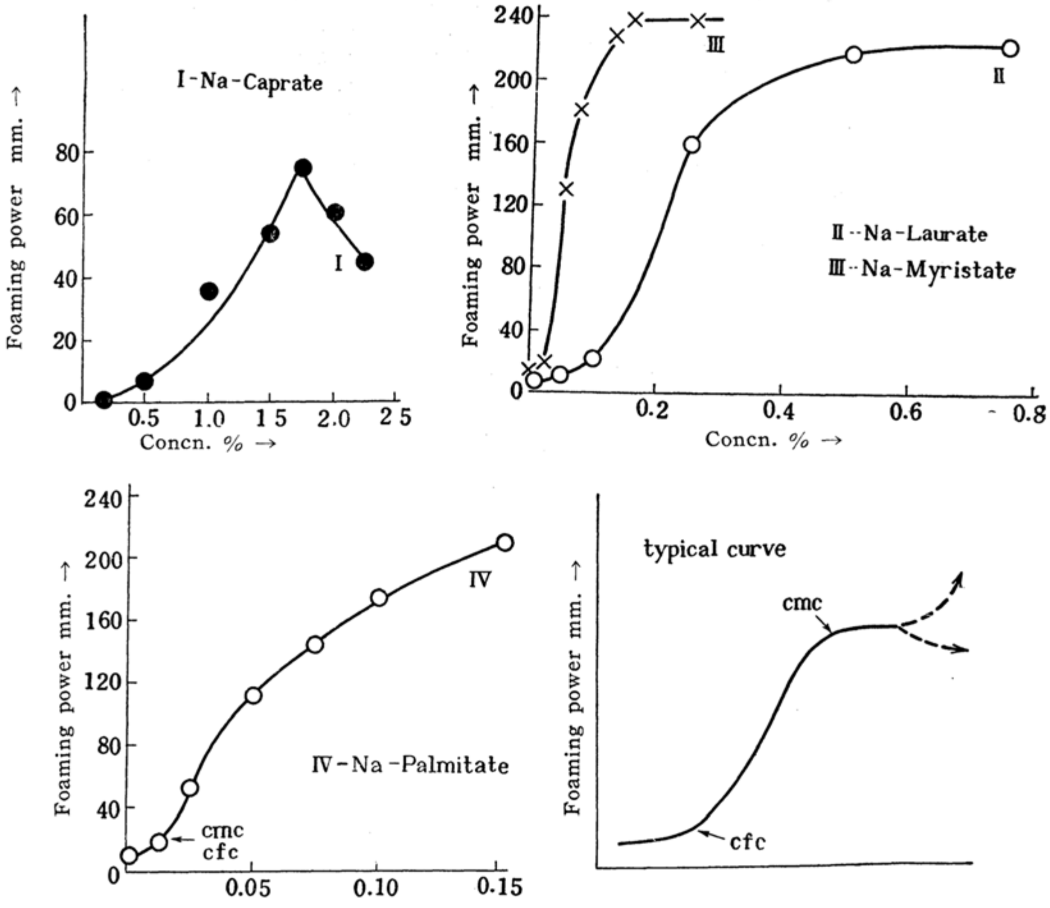

Fig. 2. Foaming power of soap.

increases, surface tension decreases and above the same cmc. both curves become practically constant.

Fig. 2 shows the foaming power of soap. As in the case of SDS already described, the tendency is again the same. The same sort of result was obtained for potassium soap by the other method; however, the method of Ross-Miles seems to be more accurate than this shaking method[4].

From the curves which appeared in Fig. 2, it was found that sodium myristate has more pronounced foaming power than others. Sodium stearate was also studied, but its foaming power was found to be too poor. Since the addition of inorganic ions is known to affect surface tension, it was thought to be interesting to add to soap neutral salts of the series lithium, sodium, potassium and rubidium chloride. Table II shows the influence of the addition of those inorganic salts on 0.1% sodium myristate.

TABLE II
INFLUENCE OF INORGANIC SALTS ON FOAMING POWER
(AVERAGE FOAMING POWER IN mm.)

Salt	Salt concn.	10^{-2} M	10^{-1} M
LiCl		244	salting out
NaCl		240	245
KCl		228	230
RbCl		228	220
None		210	210

It is demonstrated that inorganic ions raise the foaming power of soap in the order $Li^+ > Na^+ > K^+ > Rb^+$.

Nevertheless, the difference between each ion at the concentration of 10^{-2} M is only slightly noticeable and ten times increase in concentration of salt did not raise the foaming power noticeably.

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[4] M. Nakagaki and K. Shinoda, This Bulletin, **27** 367 (1954).

Discussion

Hobbs[5] derived the following expression by thermodynamic consideration of micelle formation from single molecule.

$$\log \text{cmc.} = -K_0\beta + \text{constant} \qquad (1)$$

Where β is the number of carbon atoms in the chain and K_0 is constant.

Empirical values of cmc. determined by the foaming power measurement as appeared in Fig. 2 are shown, together with some constants from the measurement, in Table III.

Those measured values of cmc. were found to fit the above equation and the constants are calculated as follows,

$$\log \text{cmc.} = -0.314\,\beta + 1.796 \qquad (2)$$

It might also be added that they are in good agreement with values determined by other methods[6].

Sodium palmitate deviates a little from the above equation, but this should be attributed to the fact that its cmc. can not be distinguished from cfc.

TABLE III
SOME PHYSICAL CONSTANTS OF SOAP

No. of carbon atoms	cmc. mol/l.	Critical* foam conc. M	Approximate expansion ratio at cmc.**
10	0.0902	0.05	19
12	0.0228	0.009	58
14	0.0049	0.001	58
16	0.0009	0.0009	28

* Critical foam concentration is defined by the author as the concentration at which foaming begins and below which foaming is negligibly small.

** Expansion ratio: V_f/V_l where V_f is the volume of foam converted from liquid state and V_l is the volume of liquid which has been converted into foam.

Although quantitative treatment has not yet been made, decrease in surface tension always seems to result in increase of foaming power as shown in Fig. 1.

For soap the same relationship seems to exist. Comparison of Fig. 2 with surface tension data of Powney and Addison[7] corresponds to this rule.

For foaming properties, the influence of ion seems to be more predominant than that of micelle, since foaming increases with concentration up to cmc. and above it becomes nearly constant. Debye[2] demonstrated through light scattering in soap solutions that, as the number of long chain ions per micelle is of the order of 100, single ionswill predominate below cmc. and above it their concentration will change only slightly. The effect of inorganic ions is in the order of lyotropic series as shown in Table II, but is only slightly noticeable. It is known that cmc. of some surfactants shifts on the addition of inorganic salts; however, change in cmc. is independent of the kind of salt, and depends only on the concentration of cation[8].

Summary

1) The foaming power measurement by Ross-Miles method was found to be useful for the study of surface active substances.

2) A general rule for the foaming power would be that it increases with concentration up to cmc., and above it, becomes nearly constant or somewhat decreases. The foaming power is also inversely proportional to the surface tension.

3) The cmc. and other physical constants can be determined by the foaming power measurement.

4) Ion rather than micelle is presumed to be predominant with respect to foaming properties.

5) Effect of inorganic ions on foaming is slightly in the order of lyotropic series, namely $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$, just before salting out.

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[5] M. E. Hobbs, *J. Phys. and Colloid Chem.*, **55**, 615 (1951).

[6] E. K. Goette, *J. Colloid Sci.*, **4**, 459 (1949).

[7] J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **34**, 372 (1938).

[8] M. L. Corrin and W. P. Harkins, *J. Am. Chem. Soc.*, **69**, 682 (1941).